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## Generation of excited CN molecules electronically desorbed from alkali-rich surfaces

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Exposure of alkali-halide crystal surfaces and alkali-metal surfaces to nitrogen- and carbon-containing gases is found to greatly enhance electron- and photon-stimulated desorption (ESD, PSD) of excited CN. The observations that the desorption yield of CN\* grows as a function of surface exposure to CO<sub>2</sub> and N<sub>2</sub> gases provide strong insight into the origin of the desorbed CN and the desorption process itself. In addition, the data unambiguously show that pre-irradiation of the alkali-halide surface by electrons or photons is required for this dose-dependent enhancement to occur. The rate of the growth is found to be correlated to the alkali component of the alkali-halide substrate. On the basis of this work we present a new model to explain electronic desorption of excited molecules from alkali-halide surfaces. The model involves three processes: (1) pre-irradiation produces alkali metal-rich surfaces via defect-mediated processes, (2) when the surface is exposed to CO<sub>2</sub> and N<sub>2</sub>, surface reactions generate CN molecules bonded to the alkali-rich surface, and (3) electron or photon bombardment induces the desorption of excited CN molecules from the surface by direct bondbreaking.

### 1. Introduction

Bombardment of alkali-halide surfaces with electrons and with UV synchrotron radiation produces optical emissions which arise from: (a) desorbed excited molecules and atoms, (b) excited bulk-impurities, and/or (c) defect recombination in the bulk material (bulk luminescence). Measurements of these spectra permit one to determine final states of excited neutral desorbates, to interrelate surface and bulk dynamical processes, and thus to elucidate mechanisms responsible for adsorption and desorption phenomena [1].

Atomic or molecular adsorbates on surfaces may originate either by the migration of atoms, molecules, or defects from inside the bulk to the surface or by the adsorption of atoms or molecules from external sources. We utilize the techniques of electron- and photon-stimulated desorption to help distinguish between these two sources of adsorbates. For example, photon-stimulated desorption of H<sup>+</sup>/ from alkali fluorides has been found to be dependent on photon-activated migration of an intrinsic hydrogen impurity to the surface [2]. For the case of ESD and PSD of Li from LiF surfaces, F-center diffusion was identified as the means by which neutral lithium is supplied to the surface [3]. In contrast, some desorption experiments require that the surface be exposed to gaseous molecules, e.g., NO [4-7],

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CO [8], OH [9] and N<sub>2</sub> [10] desorption from metal surfaces. We note also that ESD and PSD studies are facilitated by knowledge of surface parent molecules.

In a previous paper, we reported first measurements of electron-stimulated desorption of excited CN from alkali halide surfaces [11]; however we did not identify the origin of the atomic components of the desorbed excited CN. As discussed above, it is conceivable that this desorbed species may originate either from migration from the bulk, or from surface dosing, or both. We are aided in this study by the fact that bulk intrinsic impurity CN<sup>-</sup> centers have been observed from measurements of CN<sup>-</sup> fluorescence under ion [12] electron and photon [13] bombardment of alkali-halides. From this information one can speculate that a possible source of surface CN adsorbates is the diffusion of these CN<sup>-</sup> impurities to the surface. However, when Nakagawa and co-workers [14] monitored CN<sup>-</sup> impurity growth in the near-surface bulk of alkali-halide crystals by observing UV fluorescence while exposing the surfaces to gaseous CO<sub>2</sub> and N<sub>2</sub> under short-wavelength synchrotron undulator light, they showed that surface CN may also migrate into the bulk. Although there may be some contribution from the bulk, our present work provides direct evidence that the exposure of alkali-halide surfaces to gaseous CO<sub>2</sub> and N<sub>2</sub> provides the primary source of adsorbates required for electron- and photon-stimulated desorption of excited CN molecules. More specifically, exposure to gaseous molecules followed by dissociation and recombination increases the surface concentration of CN which acts as a source of CN<sup>\*</sup> desorption.

Formation of adsorbates by the dissociation of large molecules or by the recombination of two individually bound atoms or molecules has been investigated in thermal desorption, and reviewed by Zacharias [16]. Modl and co-worker [15] found that NO observed in thermal desorption arises from the decomposition of NO<sub>2</sub> on a Ge(111) surface. On the another hand, H<sub>2</sub> formation was found to be due to the recombination of atomic hydrogen on a Cu(110) surface [17], and the source of CO in thermal desorption to be the recombina-

tion of carbon and oxygen bound to a Pd(100) surface [18]. The present work suggests that the formation of adsorbates which participate in the ESD and PSD of excited CN from alkali-halide crystals and alkali metals proceeds by a reactive mechanism involving both dissociation and recombination processes.

Incident electrons or photons may also stimulate surface processes (adsorption, dissociation, recombination, and desorption) by creating bulk and surface defects, changing surface stoichiometry, modifying the surface structure, and breaking bonds on the surface. Electron-stimulated adsorption (ESA) [19], an enhancement of adsorption initiated by electron irradiation, can be an important step in surface reactions. ESA and its relation to surface reactions have been reviewed by Pantano and Madey [20]. Photon-induced rupture of bonds on surfaces appears to play an important role in photon-stimulated processes involving adsorbates on surfaces. Unfortunately, very little is as yet known, either experimentally [21] or theoretically [22], about photodissociation on solid surfaces. It is therefore of great interest to investigate other radiation-altered surface processes as well as stimulated desorption.

We report below new measurements which for the first time link electron- and photon-stimulated desorption (ESD and PSD) of excited CN molecules from alkali-halide and alkali-metal surfaces to the exposure of these surfaces to gaseous CO<sub>2</sub> and N<sub>2</sub>. The results show that the desorption yield grows as a function of the exposure of these surfaces to the gaseous molecules, and that the growth is strongly enhanced by pre-irradiation of the alkali-halide surface. The data indicate that incident electron and UV photon radiation serve two important functions: (1) incident radiation metallizes the alkali-halide surfaces which significantly enhance the surface CN formation process upon subsequent gas exposure, and (2) incident radiation leads to direct scission of the surface-CN bond. These measurements give information on the dynamics of making and breaking of bonds on surfaces and provide insight into related technological applications such as surface catalysis, erosion, surface damage, and lithography.

## 2. Experimental details

The experimental setup, shown in fig. 1, consists of an ultrahigh vacuum (UHV) system, which operates at a base pressure about  $3 \times 10^{-10}$  Torr. The incident radiation was either electrons or synchrotron radiation. The samples were alkali-halide crystals and alkali metals which could be heated or cooled.

Used was a low-energy, high-brightness electron gun consisting of a diode extraction source and a three-element refocusing lens, similar to the design of Stoffel and Johnson [23]. A heated osmium-coated dispenser cathode emitted electrons with an energy spread of 0.1 to 0.2 eV. The electron beam energy was adjustable in the range of 10 to 1000 eV, with electron current ranging from 20 to 400  $\mu$ A. The beam diameter varied from 1.5 to 5 mm.

The photon measurements were carried out at the University of Wisconsin Synchrotron Radiation Center (SRC) using the Vanderbilt/SRC joint beamline. The beamline features a computer controlled 6-meter toroidal grating monochromator delivering dispersed light in the range from 9 to 190 eV. A differential pumping station is located between the beamline and the experimental chamber resulting in a 5 orders of magnitude difference of pressures between the beam

line and the working chamber. At the plane of the sample, the beam spot was 2.7 mm high by 7.4 mm wide. A 93% transparent nickel mesh was mounted in the beamline and used to measure the beam flux.

The alkali-halide crystals were purchased from Harshaw. The crystals were cleaved in air, mounted with their (100) surfaces facing the beam and heated under UHV conditions for cleaning. Alkali-metal surfaces were obtained by evaporation from SAES alkali dosers onto a glass slide. To obtain thick metal layers, we continued the dosing until there was no optical transmission. These evaporated surfaces are referred to hereafter as alkali-metal surfaces. The sample temperature could be varied from 58 to 800 K. An XYZ-adjustable closed-cycle helium cooler was used for low-temperature experiments. A piece of sapphire was mounted between the sample holder and the cold finger, since sapphire has a high heat conductivity at low temperatures (70 K), and is thermally insulating at high temperatures ( $> 300$  K). A chromel–alumel thermocouple, placed in thermal contact with the sample surface, measured temperatures greater than room temperature, and a chromel–gold thermocouple was used for temperatures lower than room temperature. Dosing gases were admitted to the chamber through two Varian leak valves allowing

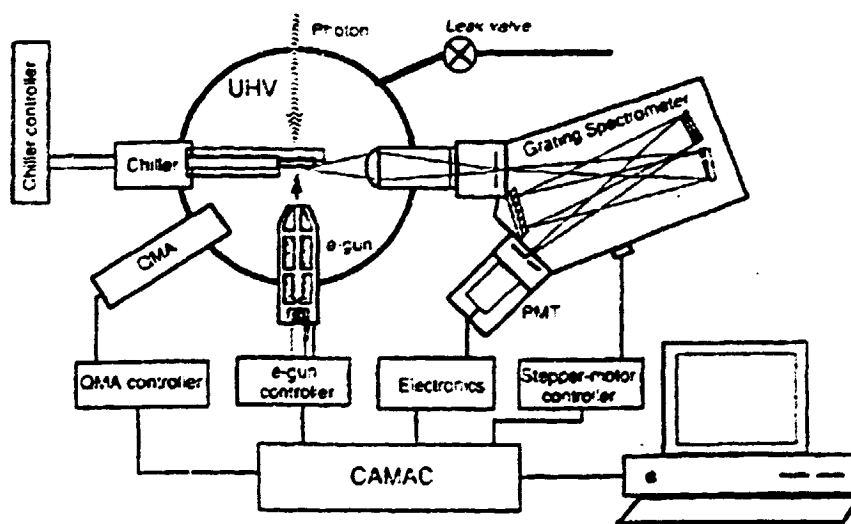


Fig. 1. Experimental configuration used for the CN desorption experiments.

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the partial pressures of two gases to be controlled in the range of  $1.0 \times 10^{-10}$  to  $1.0 \times 10^{-6}$  Torr.

Optical emissions from the samples due to electron or photon bombardment were imaged onto the entrance slit of a McPherson 0.3-m monochromator. A 1200 lines/mm grating (5000 Å blaze) was used for fluorescence measurements from 2000 to 8000 Å; and a 2400 lines/mm grating (3000 Å blaze) was used to measure the rotational distribution of the desorbed CN\* molecule. Photons were detected by a cooled photomultiplier tube (PMT), operated in a pulse-counting mode. Stepping motor grating controls and photon counting scalars were interfaced through a CAMAC unit to an Apple Macintosh computer. A quadrupole gas analyzer (QMA) was used to detect residual gas, dosing gas, and outgasing due to desorption.

### 3. Results

#### 3.1. Optical emission due to electron and photon bombardment

Bombardment of alkali-halide surfaces with electron or synchrotron radiation produces optical emissions arising from defect recombination in the bulk, from excited bulk-impurity molecules, and from desorbed excited molecules and atoms. These three features are shown prominently in fig. 2 which is a 2000–8000 Å spectrum from KCl

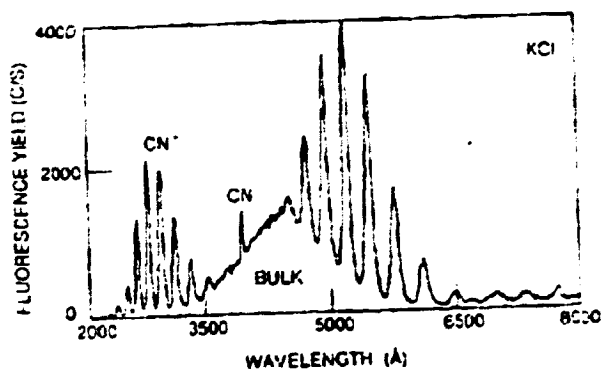


Fig. 2. Typical optical emission spectrum in the range 2000–8000 Å due to zero-order synchrotron light bombardment on a single crystal KCl surface at room temperature. The surface was exposed to gaseous  $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr.

under synchrotron light bombardment at room temperature.

The continuous fluorescence in the range of 3500 to 5500 Å is luminescence accompanying defect recombination [24]. The nine bands between 2000 and 3500 Å (observed here also in second order) is due to optical emission from excited  $\text{CN}^-$  impurities in the near-surface bulk [25]. By noting the energy of the emitted photons, we have determined that the observed  $\text{CN}^-$  excited state is at least 5.6 eV above the ground state. If the  $\text{CN}^-$  molecules were in the gas phase, this energy would be large enough to reach the gas-phase ionization limit of 3.8 eV [26]. Thus the gas-phase  $\text{CN}^-$  excited state would result in neutralization ( $\text{CN} + e$ ) rather than de-excitation by optical emission as observed. However in alkali-halide lattices, the ionization potential of  $\text{CN}^-$  is raised to about 10 eV [27]. For this case, the neutralization channel is not available. Instead optical de-excitation provides a readily available relaxation channel for excited  $\text{CN}^-$  impurities in bulk alkali halides in agreement with experimental results.

The narrow band feature at approximately 3870 Å arises from excited CN desorbed from the KCl surface. This feature was identified in ref. [11] as the  $\text{CN } B^2\Sigma^+ \rightarrow X^2\Sigma^+$  transition. This characteristic emission attributed to the decay of a free excited  $\text{CN}^*$  molecule above the surface has been also observed for LiF, NaF, NaCl, KBr, and CsI crystals, and for lithium-, sodium-, potassium-, and cesium-metal surfaces, under electron bombardment.

Optical radiation arising from above the surface can be distinguished from bulk radiation by measurements of the spatial location of the emission, as shown in fig. 3. This figure is a plot of the intensities of optical emissions from  $\text{CN}^*$ , from  $\text{CN}^-$  radiating in the bulk, and from other bulk excitations versus the position of the image of the 300- $\mu\text{m}$  spectrometer slits as the sample is translated along the beam direction. The emission arising from the  $\text{CN}^-$  impurity and the bulk fluorescence appears along the whole crystal, with an enhancement on the front and rear faces of the sample. The distance between the two peaks matches the thickness of our sample, 2.2 mm. In

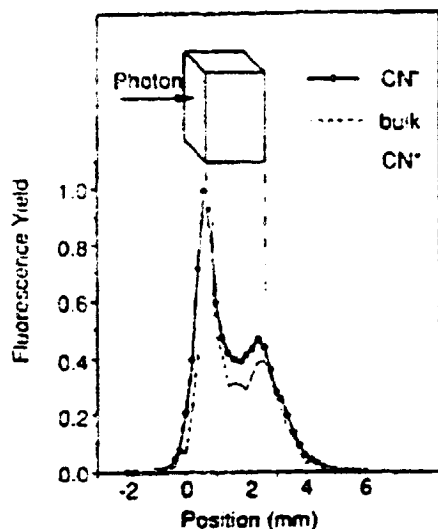


Fig. 3. Position dependence of optical emission arising from  $\text{CN}^*$ , bulk impurity center  $\text{CN}^{*-}$  and bulk fluorescence due to zero-order synchrotron light bombardment on a single crystal KCl surface at room temperature. The surface was exposed to gaseous  $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr. The x-axis is the manipulator reading representing the distance between the optics focus region and the front surface of the sample.

contrast, the optical emission from neutral excited CN can be seen only in front of the surface. This confirms that the  $\text{CN}^*(\text{B})$  radiation arises from just above the surface.

### 3.2. Enhancement of $\text{CN}^*$ ESD yield due to $\text{CO}_2$ and $\text{N}_2$ exposure

Fig. 4a shows the time-dependent growth of excited CN desorption yield under 110  $\mu\text{A}$ , 200 eV electron bombardment on KBr(100) surfaces as the surface was exposed to gaseous  $\text{N}_2$  at two dosing pressures,  $2.0 \times 10^{-8}$  and  $5.7 \times 10^{-8}$  Torr. The plot is the  $\text{CN}^*$  emission yield versus the exposure time at a constant  $\text{N}_2$  pressure. The surface was irradiated by a beam of 200 eV electrons for four hours prior to gas dosing. Note that the  $\text{CN}^*$  desorption yield grows with the exposure time and that the growth tends to saturate at a level characteristic of the pressure. The growth of the electron-induced  $\text{CN}^*$  desorption yield under gaseous  $\text{N}_2$  exposure has also been investigated for KCl and LiF surfaces, as shown

in figs. 4b and 4c. The desorption yields for all surfaces show a similar monotonic increase with  $\text{N}_2$  gas exposure but differ with regard to the time to reach saturation. The rise times, defined as the time to reach 90% of the saturation yield, are 20 min for KCl, 19 min for KBr and about 40 min for LiF. Note that the time constants for KBr and KCl surfaces are essentially the same, but markedly different from that for the LiF surface. This correlation suggests that the parent bond from which desorbed  $\text{CN}^*$  arises is the the bond between surface metal and CN where for these measurements, the metal is either lithium or potassium.

In another experiment, a KCl surface, bombarded by 300-eV electrons at a constant current

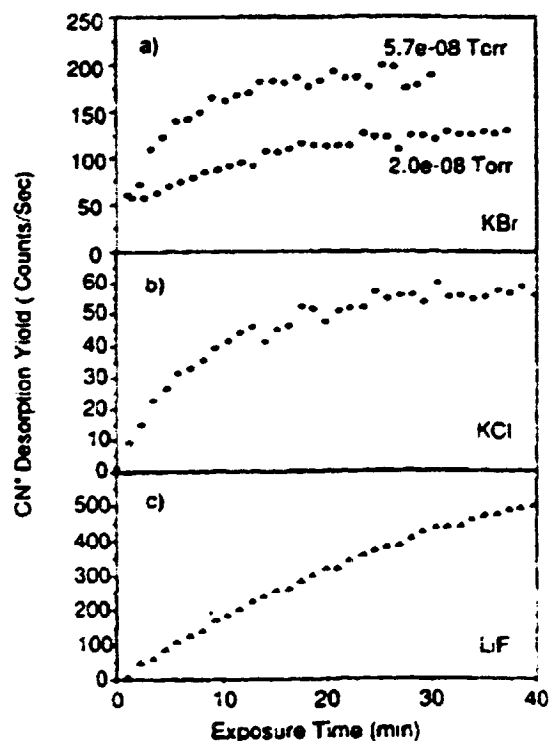


Fig. 4. Growth curves of  $\text{CN}^*$  desorption yields as a function of time during gas exposure and electron-beam dosing: (a) KBr sample exposed to gaseous  $\text{N}_2$  at  $2.0 \times 10^{-8}$  Torr and  $5.7 \times 10^{-8}$  Torr under 110  $\mu\text{A}$ , 200 eV electron bombardment, (b) KCl sample exposed to gaseous  $\text{N}_2$  at  $5.0 \times 10^{-8}$  Torr and (c) LiF sample exposed to gaseous  $\text{N}_2$  at  $5.3 \times 10^{-8}$  Torr under 100  $\mu\text{A}$ , 200 eV electron bombardment. Substrate temperature for these experiments was 60 K.

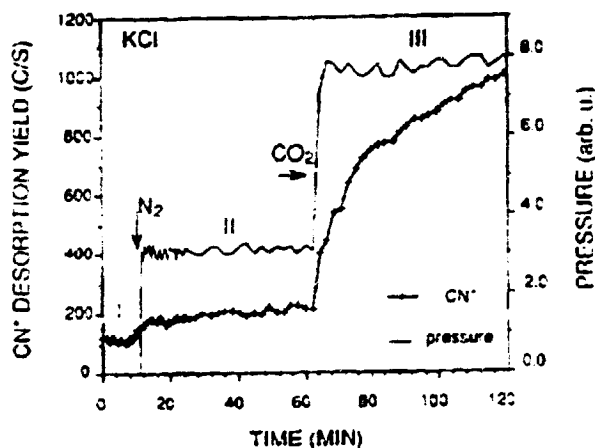


Fig. 5. The  $\text{CN}^*$  desorption yield measured for a given KCl surface as a function of time under various gas exposure conditions: (I) a clean KCl surface, (II) the same KCl surface exposed to  $\text{N}_2$  ( $1.2 \times 10^{-8}$  Torr) and (III) the KCl surface additionally exposed to  $\text{CO}_2$  ( $3.2 \times 10^{-8}$  Torr). The lighter solid line is a plot of total pressure as a function of time. The incident electron beam energy was 300 eV with a constant current of 100  $\mu\text{A}$ . Substrate temperature for this experiment was 60 K.

of 100  $\mu\text{A}$ , was dosed sequentially first by  $\text{N}_2$  and then by  $\text{CO}_2$ , as shown in fig. 5. This figure is a plot of  $\text{CN}^*$  emission yield (dark line) and gas pressure (weak line) as a function of time. Initially, there was no external gas introduced into the chamber. Under these circumstances a small, constant  $\text{CN}^*$  desorption yield was observed. When the surface was exposed to gaseous  $\text{N}_2$  at a constant pressure of  $1.2 \times 10^{-8}$  Torr (beginning at the time indicated by the first arrow), the  $\text{CN}^*$  desorption yield increased toward saturation. Later, the surface was exposed to gaseous  $\text{CO}_2$  at a constant pressure,  $3.2 \times 10^{-8}$  Torr, concurrent with  $\text{N}_2$  exposure. As shown in the figure, the  $\text{CN}^*$  desorption yield increased dramatically. The ratio of the saturation yields attributable to the combined  $\text{CO}_2$  and  $\text{N}_2$  gas exposures is 8.9, which is significantly larger than the ratio of partial pressures of  $\text{CO}_2$  and  $\text{N}_2$ , which is 1.7. This indicates that simultaneous dosing of  $\text{CO}_2$  and  $\text{N}_2$  gases results in a significantly higher  $\text{CN}^*$  desorption yield than  $\text{N}_2$  dosing alone. We observe similar effects for KBr and LiF substrates. Thus we find that the  $\text{CN}^*$  desorption yield markedly increases when alkali-halide surfaces

are exposed to gaseous  $\text{N}_2$  and  $\text{CO}_2$  under electron or photon irradiation. In addition, we believe that the small yields measured under conditions of no external dosing are due to residual  $\text{N}_2$  and  $\text{CO}_2$  gases normally in the chamber even under ultrahigh vacuum conditions.

### 3.3. Enhancement of $\text{CN}^*$ PSD yield due to $\text{CO}_2$ and $\text{N}_2$ exposure

Fig. 6 displays optical spectra arising from zero-order synchrotron radiation incident on a glass surface, with and without a thick layer of potassium metal, and with and without  $\text{CO}_2 + \text{N}_2$  exposure. Initially the clean glass sample was bombarded by photons *in situ* for 20 min; fig. 6a shows the resulting optical emission. The continuous fluorescence is due to recombination of defects created by photon bombardment in the glass [28]. Next, potassium was evaporated onto

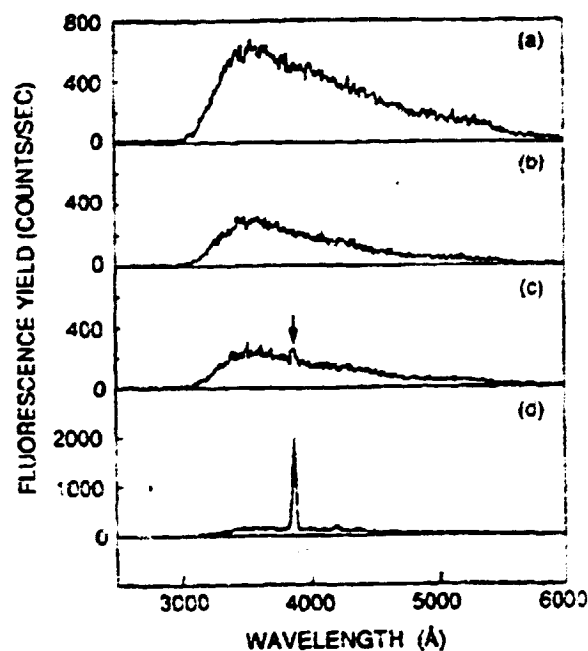


Fig. 6. Optical emission spectra due to zero-order synchrotron light bombardment (a) on a clean piece of glass, (b) on a potassium-covered glass surface, (c) on a potassium-covered surface with exposure of the surface to gaseous  $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr for 2 min, and (d) on a potassium-covered surface following gas exposure ( $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr) for 30 min at room temperature.

the surface. The resulting optical emission spectrum is shown in fig. 6b, where the bulk fluorescence intensity is reduced due to the presence of the potassium layer. Then the potassium-covered surface was exposed for two min to a one-to-one mixture of  $\text{CO}_2 + \text{N}_2$  at a pressure of  $1.0 \times 10^{-7}$  Torr. The resulting spectrum, fig. 6c, shows a feature at  $3870 \text{ \AA}$  which we attribute to the decay of desorbed  $\text{CN}^*$ . Finally, after 30 min of the  $\text{CO}_2 + \text{N}_2$  (1:1) exposure with simultaneous photon irradiation, the intensity of the characteristic line is markedly enhanced as shown in fig. 6(d). We can conclude from these measurements that photon-stimulated  $\text{CN}^*$  desorption is greatly increased with  $\text{CO}_2 + \text{N}_2$  exposure. On a clean glass surface,  $\text{CN}^*$  desorption was not observed under photon bombardment and simultaneous  $\text{CO}_2 + \text{N}_2$  exposure. Similar enhancement of  $\text{CN}^*$  desorption yields due to  $\text{CO}_2 + \text{N}_2$  exposure were observed from KCl, and from sodium- and lithium-covered glass surfaces.

### 3.4. The role of pre-irradiation in the enhancement of $\text{CN}^*$ desorption yield

Three additional experiments were performed which show that the marked increase in the  $\text{CN}^*$  desorption yield is observed only after the alkali-halide surface is pre-irradiated with electrons or photons.

The first experiment determined the dependence of the  $\text{CN}^*$  desorption yield on the samples' radiation history. The results are shown in fig. 7, for the case of 300-eV electron bombardment of KCl surface at 60 K.  $\text{CN}^*$  desorption yield measurements were made for a wide range of pre-radiation doses (defined as the pre-radiation time multiplied by the electron current in units of  $\mu\text{A h}$ ). The  $\text{CN}^*$  desorption yields, plotted as a function of the exposure time, reach saturation values which are strongly dependent on the pre-radiation dose. The inset in fig. 7 shows that the saturation values plotted as a function of pre-irradiation dose tend toward saturation. For a typical current of  $130 \mu\text{A}$ , nine hours were required to reach saturation, as shown in fig. 7.

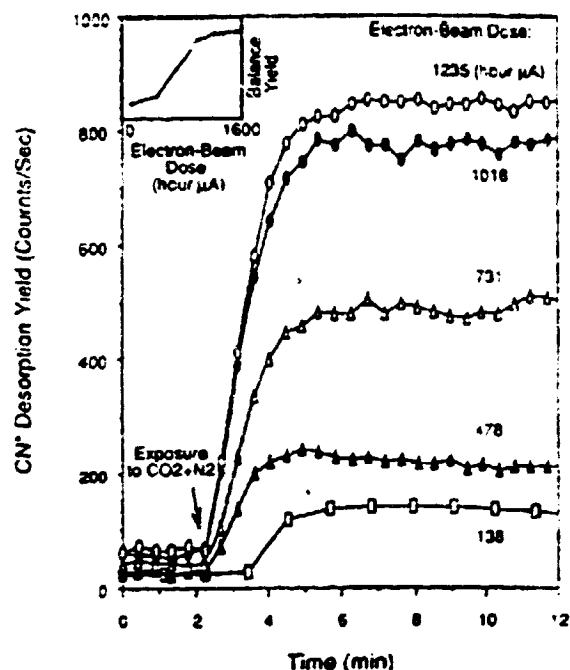


Fig. 7.  $\text{CN}^*$  desorption yields from a KCl surface at 60 K plotted as a function of time exhibiting the influence of gas exposure,  $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr, for a variety of electron-beam integrated doses.

The second experiment involved a measurement of the difference in the  $\text{CN}^*$  PSD yield for a KCl surface with and without pre-irradiation. Desorption was measured under zero-order synchrotron light bombardment at 300 K and with exposure to gaseous  $\text{N}_2$  and  $\text{CO}_2$ . Fig. 8a shows the time-dependent yield after 18 h of pre-irradiation by zero-order synchrotron light prior to the gas exposure. Fig. 8b shows the yield obtained with no pre-irradiation. Except for the radiation history, both experiments were carried out under the same conditions, yet the saturation rise time for the pre-irradiated sample is smaller by a factor of approximately three.

The third experiment involved a measurement of the difference between the  $\text{CN}^*$  desorption yield for a spot pre-irradiated by 300-eV electrons and the yield for the rest of the sample, which had no radiation history (fig. 9). A KCl sample was cleaved in air and annealed at  $450^\circ\text{C}$  in UHV for four h before the surface was cooled to 60 K. A single spot on the surface was pre-



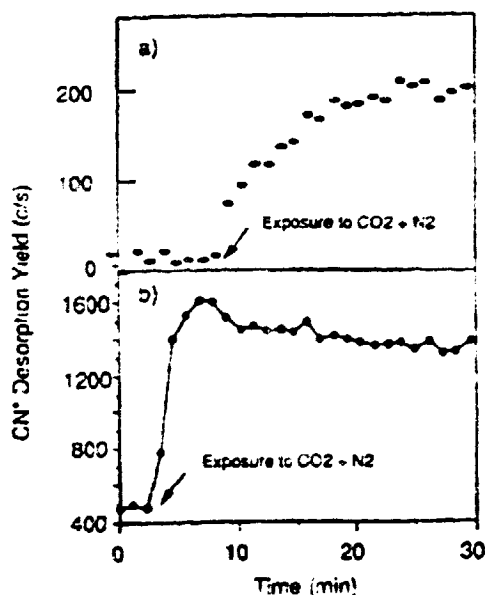


Fig. 8.  $\text{CN}^*$  desorption yields from KCl surfaces with and without photon pre-radiation at room temperature under zero-order synchrotron light bombardment in the presence of  $\text{CO}_2 + \text{N}_2$  (1:1) at  $1.0 \times 10^{-7}$  Torr. (a)  $\text{CN}^*$  desorption yield for a KCl sample plotted as a function of time for no prior synchrotron light dosing. For this measurement gas exposure commenced at the 9 minute mark. (b)  $\text{CN}^*$  desorption yield for a KCl sample plotted as a function of time which prior to this measurement had experienced 24 h of synchrotron light dosing. Gas exposure commenced at the 3 min mark.

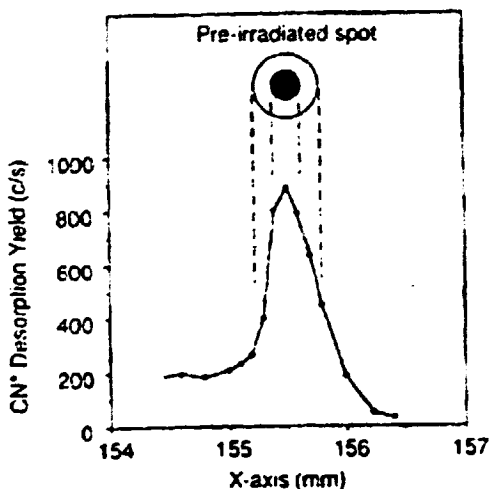


Fig. 9.  $\text{CN}^*$  desorption yields plotted as a function of distance for a path directed along a KCl sample surface. The path of measurement on the surface intersects a spot pre-irradiated by 300 eV electrons at a current of 80  $\mu\text{A}$  for 12 h. The rest of the sample had not previously been irradiated.

irradiated by 300-eV electrons for 12 h; and the surface was then exposed to gaseous  $\text{CO}_2$  and  $\text{N}_2$  at a combined pressure of  $1.0 \times 10^{-7}$  Torr. The measurements of the position-dependent desorption yields began after the desorption yields reached saturation. The  $\text{CN}^*$  desorption yield exhibited a maximum at the center of the pre-irradiated spot. Note that the yield greatly lessened as the electron beam moved to regions of the surface of the sample which had little or no previous electron-beam radiation history.

In addition, we have observed that pre-irradiation of a sodium-metal surface by an electron beam does not enhance the  $\text{CN}^*$  yield, whereas the pre-irradiation of a NaCl surface clearly enhances the  $\text{CN}^*$  desorption yield. All of these experiments indicates that the pre-irradiation produces alkali-metal-rich surfaces on alkali-halide crystals.

## 4. Discussion and conclusion

### 4.1. Surface metallization

Our data strongly suggest that surface metallization is required for CN formation on alkali-halide surfaces. As shown above in Figs. 7, 8, and 9, the formation of CN on alkali-halide surfaces requires pre-irradiation by either electrons or photons. Incident electron or UV photon radiation not only serves to stimulate the desorption of excited CN but also plays a role in preconditioning the alkali-halide surfaces for subsequent CN formation. It is extensively documented that electron [29–31] and photon [32] bombardment can induce the accumulation of excess metal on alkali-halide surfaces. Thus, we believe that there is a crucial relationship between the process of radiation-induced metallization of alkali-halide surfaces and the concentration of surface CN leading to  $\text{CN}^*$  desorption.

Surface metallization is understood in this work as a defect-mediated process. Incident photon or electron bombardment deposits energy in the near surface bulk by hole creation [33]. This deposited energy may generate a Frenkel pair, which consists of a halogen vacancy with an electron (F-

center) and a (halogen) $_2^-$  molecular ion (H-center), either in the near surface bulk or on the surface [34]. Halogen atoms, originating at the surface H-centers, may be emitted from the surface [35]. The F-centers remaining on the surface neutralize excess metal ions left following the halogen emission. Thus, electron or photon bombardment on an alkali-halide surface produces surface metallization.

#### 4.2. CN formation on alkali-rich surfaces

Our data show that the electron- and photon-stimulated CN\* desorption yields grow with surface exposure to CO $_2$  or/and N $_2$  gas. The desorption yields are a function of the concentration of the parent adsorbate (this function is complicated since adsorption sites, coadsorbates, defects, and diffusion may all affect the desorption yields). Thus, our experimental results imply that the amount of CN adsorbed on the surface grows with CO $_2$  and N $_2$  exposure. In addition, we have observed a small amount of CN\* emission from the surface under ultrahigh vacuum conditions. In fact, CN\* emission in the absence of external dosing was observed to increase when residual gas pressure increased. Because of the observed enhancement of CN\* desorption yield due to CO $_2$  and N $_2$  dosing, we believe that the CN\* desorption from alkali-halide surfaces in the absence of external dosing [11] arises from residual CO $_2$  and/or N $_2$  gases.

Formation of molecular adsorbates can occur either from dissociation of large molecules on surfaces [16] or from the recombination of two individually bound atoms [17,18]. The present work suggests that the CN formation process on alkali-halides involves molecular dissociation on the surface followed by recombination. In the dissociation process, CO $_2$  and N $_2$  molecules decompose on the pre-irradiated surfaces into their constituent atoms. Next is the recombination of these atoms into a new molecule which includes CN as one of its constituent parts.

An important question is what is the identity of the bond present on the pre-irradiated alkali-halide surface prior to CN\* desorption. Our data provides evidence that there is a definite correla-

tion between the presence of surface metal and the characteristics of electronically desorbed CN\*, which strongly suggests that the parent bond of the desorbing CN\* is the ionic bonding between surface alkali and CN molecule. Three important classes of measurements support this conclusion.

The first class of measurements discussed above, relates the rise-time of electronically desorbed CN\* (which is related to surface CN concentration) to the alkali component of alkali halide, as shown in fig. 4. Clearly, the halide component is not important.

The second class of experiments described in ref. [36] shows that the rotational distributions of desorbing CN\* are systematically correlated to alkali components of alkali-halide and alkali-metal substrates. Alkali metals and alkali-halides with the same alkali component, give rise to the same rotational distribution. The distribution is found to be independent of the halide component of the substrates.

The third class of experimental evidence is that the excitation function of desorbing CN\* by photons exhibits resonance structure (16 and 20 eV) for both potassium metal and KCl surfaces, independent of the chloride component of KCl substrate [36].

In all these cases, there exists a strong systematic correlation between the alkali component and the desorbing CN\* which suggests that CN is bonded to the surface alkali.

#### 4.3. Mechanism for the desorption of excited CN

As shown above, the presence of alkali-CN on the surface is essential to the desorption phenomena observed. Also, the data suggest that the mechanism responsible for breaking the bond of alkali-CN is desorption induced by electronic transitions (DIET) [37]. Specifically, the parent alkali-CN is excited electronically from its bound state to an anti-bonding state.

An important question is the nature of the anti-bonding state participating in the observed desorption of excited CN in the B state. The B state of neutral CN may be formed directly by the  $4\sigma \rightarrow 5\sigma$  excitation of the CN molecule or by the

$4\sigma$  ionization of ground state  $\text{CN}^-$ . Our present results cannot determine whether the surface CN is bonded to one or two or possibly more metal atoms (e.g.,  $\text{K}_n$ ). However, it is reasonable to assume that the alkali-CN bond is primarily ionic, and hence that the  $4\sigma$  ionization channel of  $\text{K}_n^+-\text{CN}^-$  system results in a  $\text{K}_n^+-\text{CN(B)}$  cationic repulsive state. As discussed in ref. [36], we observed a resonance peak at 16 eV in the photon energy dependent yield of desorbing  $\text{CN}^*$  from a potassium metal surface, which is close to the calculated value (17 eV) of the  $4\sigma$  ionization energy for a similar system, CN adsorbed on Ni metal [39]. These considerations suggest that the  $\text{K}_n^+-\text{CN}^-$  system is raised to an antibonding  $(\text{K}_n\text{CN})^+$  state by the ionization of the  $\text{CN}^-$   $4\sigma$  state, and the desorption of CN in the B state results.

Another possible channel for surface CN loss in addition to desorption is that  $\text{CN}^-$  may diffuse from the surface into the near surface bulk. In order to test this hypothesis, we measured the characteristic  $\text{CN}^-$  UV radiation arising from the near surface bulk, which was observed to increase with exposure to gaseous  $\text{CO}_2 + \text{N}_2$  under synchrotron UV photon bombardment. This observation is consistent with Nakagawa and co-worker's earlier observation [14]. Consequently, it is clear that an important source of the  $\text{CN}^-$  impurity in the near-surface bulk is surface exposure to gaseous  $\text{CO}_2 + \text{N}_2$ . This indicates that surface CN, probably in the form  $\text{K}_n^+-\text{CN}^-$ , is an important intermediate step in the formation of  $\text{CN}^-$  impurities in the near surface bulk just as it is an important intermediate step in the desorption process.

In conclusion, the origin of ESD and PSD of excited CN from alkali-metal and pre-irradiated alkali-halide surfaces has been found to be intimately related to exposure of the surfaces to  $\text{CO}_2$  and  $\text{N}_2$  gases. For alkali-halide surfaces, electron- and photon-induced metallization of alkali-halide surface is required for alkali-CN formation. The data suggest a new desorption model which can be described as a three-step process: (1) pre-irradiation of alkali-halides results in alkali-metal-rich surfaces via a defect-mediated process, (2) a surface reaction produces alkali-CN

molecules on the surface when the alkali-rich surface is exposed to  $\text{CO}_2$  and  $\text{N}_2$  prior to desorption, and (3) an electron or photon bombardment breaks the  $(\text{alkali})^+-\text{CN}^-$  bond and induces electronic desorption of excited CN molecules from the surface.

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